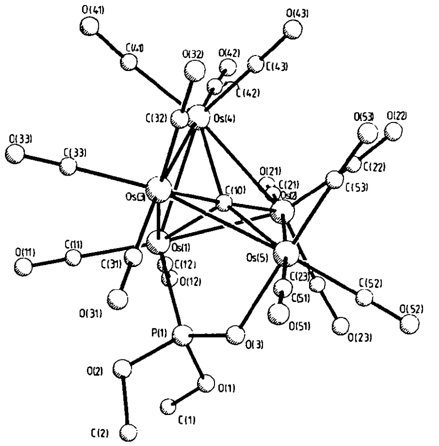

Fig. 2. $HOs_5C(CO)_{14}[OP(OCH_3)_2]$, showing the atom numbering.

Å). Os(1)—P(1) and P(1)—O(3) are shorter than would be expected for pure σ bonds, while Os(5)—O(3) is long. Similar trends have been observed in the Ru—P—O—Ru system of $HRu_2(CO)_3[P(OC_6H_4)(OPh)_2]_2[OP(OPh)_2]$ (Bruce, Howard, Nowell, Shaw & Woodward, 1972), and the short bonds have been explained in terms of π interactions.

The CO groups are all linear, and the mean Os—C and C—O lengths of 1·900 and 1·15 Å, respectively, are in good agreement with the 1·89 and 1·16 Å for $Os_5(CO)_{16}$ (Reichert & Sheldrick, 1977).

We thank the Science Research Council for financial support. Calculations were performed with the Cambridge University IBM 370/165 computer and programs written by GMS.

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Acta Cryst. (1978). B**34**, 1997–1999

Potassium Dicyano[(dithionitrito-*S*)amido]nickelate(II)

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(*Received* 5 *December* 1977; *accepted* 20 *January* 1978)

Abstract. $K[Ni(CN)_2HN_2S_2]$, monoclinic, $P2_1/c$, a = 4·203 (2), b = 18·286 (2), c = 10·440 (2) Å, β = 95·64 (3)°, V = 798·5 Å^3, Z = 4, D_x = 2·04 g cm^{-3}. Refined to R = 0·065 for 1452 observed reflexions. The Ni is coordinated in a square-planar manner by the C atoms of the CN groups and one S and one N atom of the S_2N_2H chelate ligand.

Introduction. There are several well-characterized complexes containing two chelating S_2N_2H ligands (Weiss, 1966; Weiss & Thewalt, 1968; Mayer & Weiss, 1978), but the title compound is the only stable anionic complex with one chelating S_2N_2H group. Only one complex containing one S_2N_2 (or S_2N_2H?) ligand has been described: $Cu(S_2N_2)X_2$, X = Cl, Br (Fluck & Goehring, 1956), but crystals could not be obtained.

The title compound was prepared as described by Weiss (1957). Suitable crystals were obtained by slow evaporation of an ethanolic solution. Lattice constants were calculated from the θ values of 37 reflexions, determined on an automatic single-crystal diffractometer (Siemens), by least squares (Berdesinski & Nuber, 1966). Intensity measurements on the Siemens diffractometer with the five-value method and θ–2θ scans with Mo $K\alpha$ radiation up to 2θ = 64° yielded 1452 observed reflexions. Reflexions with $I < 2·58\sigma(I)$ were classified as unobserved. The intensities were corrected for Lorentz and polarization factors only.

Atomic parameters (excluding H) were taken from an earlier determination (Müller, 1968), based on relatively inaccurate photographic data from a cleaved twin. The H atom could be located in a difference map. Full-matrix least-squares refinement with anisotropic temperature factors (for H, fixed isotropic $B = 3{\cdot}0$ Å^2) converged with $R = 0{\cdot}065$. Atomic parameters are listed in Table 1.*

Calculations were performed on an IBM 370/168 computer with the XRAY system (Stewart, Kundell & Baldwin, 1970) and scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. The complex anion and the numbering scheme are shown in Fig. 1; bond lengths and angles are summarized in Table 2.

Bond lengths and angles within the chelating group correspond to those found in $Ni(S_2N_2H)_2$ (Mayer & Weiss, 1977) and derivatives (Weiss & Ziegler, 1966; Weiss & Thewalt, 1966, 1967; Thewalt, 1970).

The Ni atom, the chelating S_2N_2H group and the C atoms of the two cyano groups lie essentially in a plane, with the two cyano N atoms sticking 0·08 Å out of it (Table 3). There is nothing unusual in the $Ni(CN)_2$ part of the anion.

Table 1. *Final atomic fractional coordinates* (×10^4)

	x	*y*	*z*
K	2691 (6)	759 (1)	601 (2)
Ni	1847 (3)	1163 (1)	2965 (1)
S(1)	1140 (8)	2299 (1)	2604 (3)
S(2)	5109 (9)	2220 (2)	4873 (3)
N(1)	3317 (27)	2697 (5)	3851 (9)
N(2)	4307 (24)	1398 (5)	4465 (8)
N(3)	7899 (23)	825 (5)	486 (8)
N(4)	2785 (26)	9529 (5)	3306 (9)
C(1)	9364 (25)	972 (5)	1446 (10)
C(2)	2440 (30)	152 (6)	3237 (10)
H	5368 (267)	1169 (62)	4989 (108)

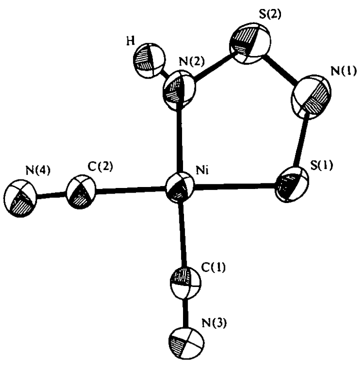

Fig. 1. *ORTEP* plot (Johnson, 1965) of the anion $[Ni(CN)_2\text{-}HN_2S_2]^-$.

Table 2. *Bond lengths* (Å) *and angles* (°)

Ni–S(1)	2·127 (3)	S(2)–N(1)	1·521 (10)
Ni–N(2)	1·841 (8)	S(2)–N(2)	1·590 (9)
Ni–C(1)	1·844 (10)	C(1)–N(3)	1·156 (13)
Ni–C(2)	1·883 (11)	C(2)–N(4)	1·151 (11)
S(1)–N(1)	1·683 (10)	N(2)–H	0·79 (11)
S(1)–Ni–N(2)	88·9 (3)	S(1)–N(1)–S(2)	119·2 (6)
S(1)–Ni–C(1)	88·6 (3)	N(1)–S(2)–N(2)	106·2 (5)
N(2)–Ni–C(2)	92·6 (4)	S(2)–N(2)–Ni	122·3 (5)
C(1)–Ni–C(2)	90·0 (4)	Ni–C(1)–N(3)	176·8 (10)
S(1)–Ni–C(2)	178·3 (5)	Ni–C(2)–N(4)	174·9 (10)
N(2)–Ni–C(1)	177·5 (4)	Ni–N(2)–H	134·1 (83)
Ni–S(1)–N(1)	103·4 (3)	S(2)–N(2)–H	103·1 (82)

Table 3. *Deviations* (Å) *of atoms from a least-squares plane*

Atoms marked with an asterisk were used to calculate the plane.

Ni*	0·011	N(2)*	0·038	N(3)	−0·079
S(1)*	0·019	C(1)*	−0·021	N(4)	−0·083
S(2)*	−0·019	C(2)*	−0·018	H	−0·018
N(1)*	−0·010				

The Ni–Ni distance corresponds to the *a* axis (4·203 Å), the interplanar distance being 3·62 Å. Thus there are no unusual intermolecular contacts. The molecular arrangement resembles that found in many 1,2-dione dioximato complexes of the metals of the Ni triad. In these cases a remarkable shortening of the metal–metal separations leading to enhanced intermolecular interactions can be achieved by oxidation (Endres, Keller, Lehmann, Poveda, Rupp & van de Sand, 1977). Thus, oxidation reactions on the title compound and related systems may be interesting.

This work was supported by the Deutsche Forschungsgemeinschaft and by the Fonds der Chemischen Industrie.

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Acta Cryst. (1978). B**34**, 1999–2000

Bis[(dithionitrito-*S*)amido]nickel(II) – A New (β) Modification

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(*Received* 5 *December* 1977; *accepted* 20 *January* 1978)

Abstract. $Ni(S_2N_2H)_2$, orthorhombic, *Pbca*, $a = 8{\cdot}390\ (1)$, $b = 12{\cdot}410\ (3)$, $c = 13{\cdot}320\ (2)$ Å, $V = 1390$ Å^3, $Z = 8$, $D_x = 2{\cdot}34$ g cm^{-3}. The structure was refined to $R = 0{\cdot}034$ for 1329 independent reflexions, and differs from the old (α) modification only in the molecular packing.

Introduction. Co, Ni, Pd, Pt form the chelate complexes $M(S_2N_2H)_2$. The structures of the last three have been determined from photographic data (Lindqvist & Weiss, 1958; Weiss & Thewalt, 1968).

The structural data were rather inaccurate and did not include H atoms. As these compounds are examples of the rare, purely inorganic chelate complexes, a redetermination of the structure of at least one of them seemed desirable. The Ni complex was prepared by varying the procedure of Goehring, Daum & Weiss (1955): 5 g of $NiCl_2.6H_2O$ and 5 g of S_4N_4 were refluxed for 1 h in 400 ml methanol. The deep-violet solution was filtered and then evaporated to complete dryness (rotator-evaporator). The residue was washed on a G3 glass frit with a large amount of cold water, until the filtrate was free from Cl^-. After drying in a desiccator it was washed with hot cyclohexane to remove S_4N_4, then dissolved in a small volume of acetone, filtered and allowed to evaporate by standing. Instead of growing the crystals from acetone, whereby the monoclinic crystals of the former structure determination were obtained, we used ethyl acetate. Lattice constants corresponded well with the known data, but insertion of the published atomic coordinates did not result in a reasonable *R*. A detailed inspection of the lattice parameters and the intensities revealed that the crystal was orthorhombic rather than monoclinic. The exact lattice parameters were calculated from the θ values of 25 reflexions, determined on an automatic single-crystal diffractometer, by least squares (Berdesinski & Nuber, 1966). Intensity measurements on the Siemens diffractometer with the five-value method, θ–2θ scans up to $2\theta = 70°$ with Mo *Kα* radiation, were carried out treating the crystal as monoclinic. Corresponding intensities were averaged to give an orthorhombic data set of 1329 independent observed reflexions, classifying reflexions with $I < 2{\cdot}58\sigma(I)$ as unobserved. The observed intensities were corrected for Lorentz and polarization factors only. The structure was solved with *MULTAN* (Main, Germain & Woolfson, 1971). H atoms were located from a difference map. Mixed refinement (isotropic temperature factors for H, anisotropic for the other atoms) converged at $R = 0{\cdot}034$.* Calculations were performed on a IBM 370/168 computer with the XRAY system (Stewart, Kundell & Baldwin, 1970). Scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

Discussion. Atomic coordinates are listed in Table 1. The asymmetric unit is formed by one complex molecule $[Ni(S_2N_2H)_2]$. The two halves of the molecule

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